INVESTIGATIONS OF CHARGED WATER DROPS

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ABSTRACT

Charged water drops were suspended in a nonuniform a.c. field and observed through the microscope visually and by high-speed photography. The initial drop size was approximately 100μ. The drop shrank by evaporation and became unstable at approximately 40μ. The evaporation of stable drops and the behavior of unstable drops were studied. The rates of changes of mass and charge were determined at various temperatures, and the activation energy for the evaporation was determined.

The evidence indicates that ions are ejected from an unstable drop, and that a burst of ions occurs in the evaporation of a stable drop under these conditions. The removal of water molecules from the evaporating drop is not rate-determining under these conditions. The drop evaporated rapidly at −26° C. and became unstable repeatedly without freezing.

1. INTRODUCTION

When a charged water drop evaporates without loss of charge, it eventually becomes unstable with respect to its spherical shape [20]. This occurs when the electrostatic surface energy exceeds the surface tension of the water. According to J. J. Thomson, the stability criterion is

$$\gamma \geqq \frac{q^2}{16\pi r^3} \tag{1}$$

when γ is the surface tension of water, q the charge, and r the radius of the drop. It has been shown theoretically by Cahn [1] that an unstable drop breaks up instantly. The reason is that a small deformation causes a local increase in electrostatic energy relative to the surface tension and thereby enhances the instability. Such a deformation may be caused by a weak electric field. Doyle, Moffett, and Vonnegut [2] reported the observation that a charged water drop virtually explodes when it reaches instability and then ejects small charged droplets. These remove approximately ⅓ of the charge but comparatively little mass from the unstable drop. As a consequence, the parent drop becomes stable. Further evaporation causes renewed instability. A large number of successive instabilities were observed. Doyle, Moffett, and Vonnegut could actually see the ejected droplets by scattered light. This indicates that they were initially stable.

In order to study these phenomena, it is necessary to suspend the drop so that it can be observed over a period of time. Doyle, Moffett, and Vonnegut suspended their drops in a uniform electric d.c. field and observed them visually by scattered light. This method takes considerable skill when using drops large enough to be seen and moving rapidly under gravity, and the lack of restoring forces makes it impossible to observe the drop through a microscope.

In order to study the behavior of charged drops in detail, we have used suspension in a nonuniform a.c. field. This method provides the restoring forces required to hold the drop in focus and in the field of view of a microscope. The observations were made visually and by high-speed photography through the microscope. This technique permits accurate measurement of the drop size from the image and, since the charge to mass ratio may be determined from the applied voltage and the position of the drop, the separate determination of size and charge as functions of time during the evaporation. Furthermore, the time resolution given by high-speed photography permits the observation of the transient behavior of unstable drops, e.g. the ejection of droplets.

The behavior of the unstable drop and the phenomena accompanying the instability were the primary subject of study in these investigations. However, in the course of the experiments it became desirable to study the evaporation of the stable drop before it became unstable, partly because the experimental technique employed permits the study of details of the normal evaporation that have not been accessible with other techniques used in the past. Such details are revealed by the time resolution and the accurate drop size determination of the photographic technique.

This paper contains a description of the experimental technique and presents some results obtained. A more detailed presentation of the subject is given in reports [17, 18] that are available upon request.

2. SUSPENSION IN A NONUNIFORM A.C. FIELD

The suspension chamber used in these experiments is shown schematically in figure 1. Two spheres are connected together and to one end of a transformer winding, the other end being connected to ground. The two spheres

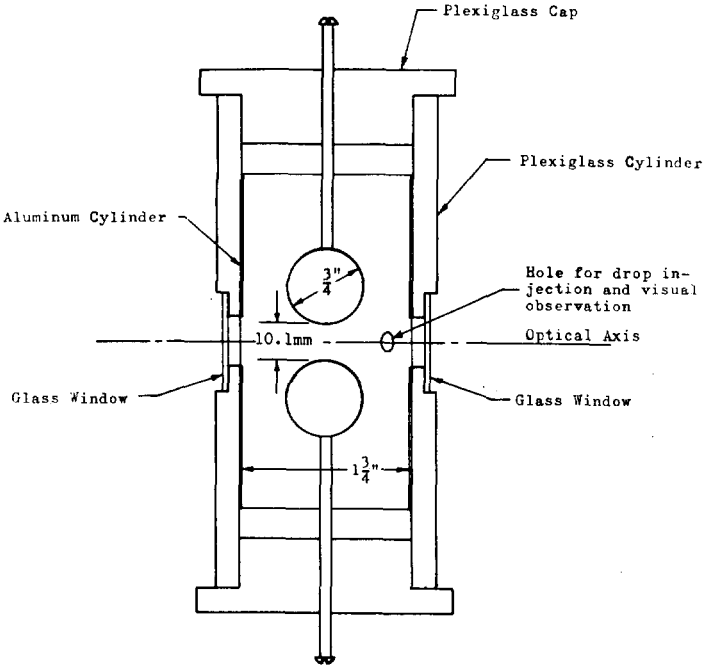

FIGURE 1.—The suspension chamber.

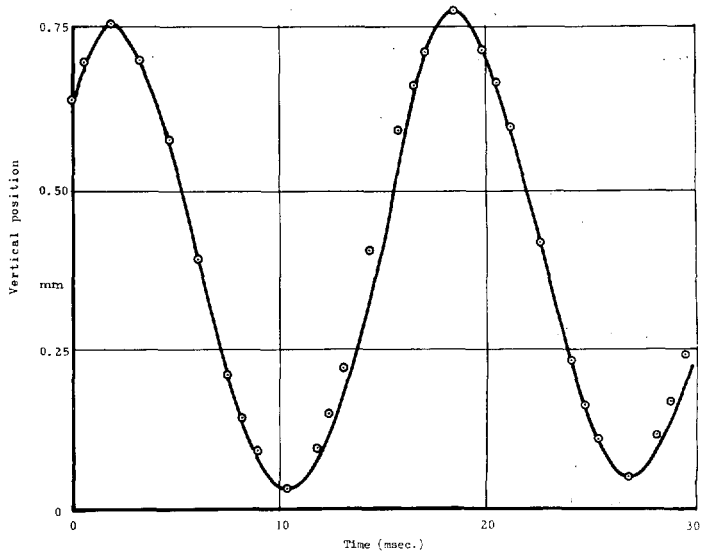

FIGURE 2.—Vertical position of an oscillating drop suspended in an a.c. field. The circles are calculated points for a sine wave of the same amplitude.

are located at the axis of a ground-connected cylinder that has holes provided for illumination and observation and for introducing the drop. The transformer is connected to the 60-c.p.s. mains.

The decisive features of this design are that it permits an unobstructed view of the suspended drop, and that it permits a great deal of versatility with respect to particle size, method of introducing and producing charged particles, and control of the atmosphere and the temperature in the chamber. An empirical determination of the field distribution showed that the field is linear over a vertical range that is adequate for the purpose at hand. This subject is discussed later on. Other investigators have used other designs with wider ranges of vertical and horizontal linearity. One such electrode configuration that has been used by Wuerker, Shelton, and Langmuir [22] is one of hyperbolic surfaces. A simpler arrangement is one with a ring instead of the cylinder in figure 1. This design has been used by Mr. Roy Schaefer of Edgewood Arsenal. It has the disadvantage that the ring obscures the drop.

It appears that Straubel is the inventor of the nonuniform a.c. field as a means for the suspension of charged particles. Straubel [21] also studied the changes in mass and charge of evaporating drops as functions of time.

The requirements on the field in our experiments are essentially as follows: (a) to keep the drop on a vertical line in focus of the microscope, (b) to give a restoring vertical force so that the drop may be caught and suspended, and (c) to give a vertical suspending field that permits the determination of the charge to mass ratio, be it by calculation or by empirical calibration of the field distribution.

Figure 2 shows the vertical position of a drop as a function of time, the position being measured from a film taken at 10,000 f.p.s. at a total magnification of 210. The points inserted in figure 2 show a sine function of the same amplitude and frequency. The actual motion deviates somewhat from the sine function with a preponderance of the second harmonic in the deviation.

The equation of vertical motion of the charged drop under these conditions is

$$m\ddot{z}+\beta\dot{z}+mg=qE\sin\omega t. \tag{2}$$

With $\zeta=z-z_0$ we have at small values of ζ

$$E=E(z_0)+\zeta\frac{\partial}{\partial z}E(z_0) \tag{3}$$

and

$$m\ddot{\zeta}+\beta\dot{\zeta}+mg=qE(z_0)\sin\omega t+\zeta q\frac{\partial}{\partial z}E(z_0)\sin\omega t. \tag{4}$$

The exact solution of this equation can be expressed in terms of Mathieu functions. The more general case with a superposed d.c. voltage applied between the two spheres and the cylinder has been treated by several investigators, e.g., [16, 19, 22] on the assumption that the field is linear, i.e., as given by formula (3). The actual motion, figure 2, shows that the Fourier expansion of the solution of the equation of motion converges rapidly. To the first approximation

$$z=z_0+A\sin(\omega t+\varphi)=z_0+A_1\sin\omega t+B_1\cos\omega t. \tag{5}$$

An analysis of the series shows that the error of this formula as compared to the exact solution is less than 4 percent under the conditions of our experiments, most of this error deriving from the neglect of the second term in the expansion. The values of z_0 and A can be expressed explicitly in terms of the constants in the equation of motion. The following notations may be used for shortness: The field constant a is defined by the formula

$$E=aVz \tag{6}$$

when V denotes the voltage applied between the spheres and the cylinder. The damping factor α is defined as

$$\alpha=\frac{\beta}{m\omega}. \tag{7}$$

In our experiments, using a water drop at 60 c.p.s. in ambient air,

$$\alpha=\frac{2.15\times10^{-6}}{r_{cm.}^2} \tag{8}$$

when the drop radius r is measured in cm., or

$$\alpha=\frac{816}{d_\mu^2} \tag{9}$$

when the drop diameter d is measured in microns. For convenience we shall put

$$b=\frac{qaV}{m\omega^2}. \tag{10}$$

In our experiments, b is approximately

$$b=\tfrac{1}{3}. \tag{11}$$

The suspension condition is that

$$\tfrac{1}{2}qaVA_1=mg \tag{12}$$

so that

$$A_1=\frac{2g}{b\omega^2}. \tag{13}$$

The corresponding formulae for B, z_0, and A are

$$B_1=\alpha\frac{2g}{b\omega^2} \tag{14}$$

$$z_0=-\frac{2g}{\omega^2}\frac{1+\alpha^2}{b^2} \tag{15}$$

$$A=\sqrt{A_1^2+B_1^2}=\frac{2g}{b\omega^2}\sqrt{1+\alpha^2}. \tag{16}$$

It turns out empirically that stable suspension and purely vertical motion requires the drop to stay below the midpoint, i.e.,

$$A<-z_0 \tag{17}$$

or

$$b<\sqrt{1+\alpha^2}. \tag{18}$$

If this condition is violated, the vertical path of the drop bends sharply into a horizontal path at the midpoint.

Formulae (15) and (16) give a simple relation between A and z_0,

$$\frac{A^2}{-z_0}=\frac{2g}{\omega^2}=0.0138 \text{ cm.}=138\mu \tag{19}$$

when $g=981$ cm./sec.^{2} and $\omega^2=(120\pi)^2$ are inserted.

Figure 3 shows a plot of observed values of A and z_0. The slope of the line through the origin is 148μ. Deducting 8 percent in order to correct for the error caused by neglecting higher terms in the Fourier expansion the slope becomes 136μ, which is close to the calculated value. This line does not hold at larger values of z_0, which indicates that the field is not linear but contains a third order term. The values of A and z_0 were kept in the initial linear region in all experiments.

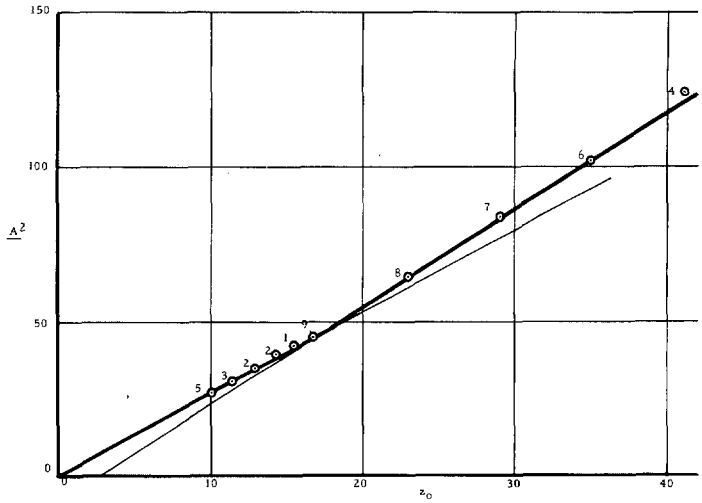

FIGURE 3.—Observed amplitude A_{obs} plotted against mean position z_0 for various drops. The figures at the points give the number of observations. 1 scale unit=55.5 μ.

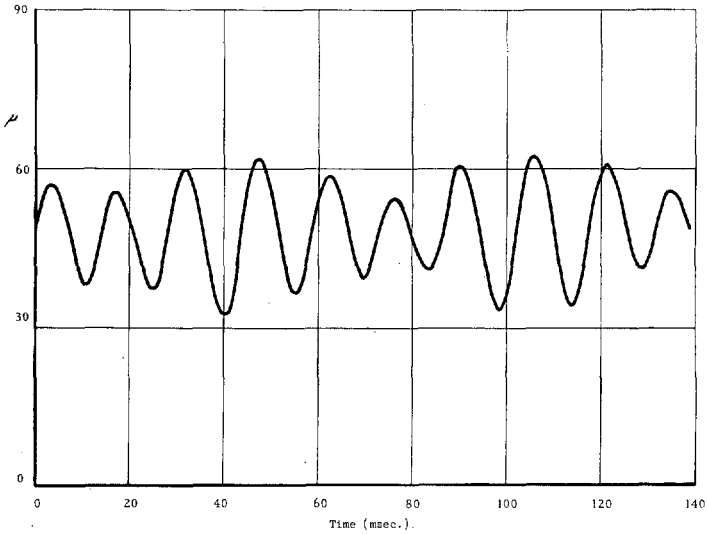

FIGURE 4.—Vertical position of an oscillating drop suspended in an a.c. field with a d.c. field between the spheres.

3. EFFECT OF A SUPERIMPOSED D.C. FIELD

When a d.c. voltage is applied between the two spheres, in addition to the a.c. voltage applied between the spheres and the cylinder, the motion of the suspended drop becomes modulated as shown in figure 4.

The vertical field in this case is

$$E=a_0V_{dc}+a'V_{dc}z^2+aV_{ac}z\sin\omega t \tag{20}$$

and the equation of motion is

$$m\ddot{\zeta}+\beta\dot{\zeta}-2qa'V_{dc}z_0\zeta-qa'V_{dc}\zeta^2+(mg-qa_0V_{dc}-qa'V_{dc}z_0^2)$$
$$=qaV_{ac}z_0\sin\omega t+qaV_{ac}\zeta\sin\omega t. \tag{21}$$

Since $z_0<0$, the force constant of the linear restoring force is positive

$$-2qa'V_{dc}z_0=m\omega_0^2 \tag{22}$$

when V_{dc} has the polarity required for lifting the drop. Putting

$$mg'=mg\left(1-\frac{qa_0}{mg}V_{dc}-\frac{1}{2}z_0\frac{\omega_0^2}{g}\right), \tag{23}$$

the equation of motion takes the form

$$m\ddot{\zeta}+\beta\dot{\zeta}+m\omega_0^2\zeta-qa'V_{dc}\zeta^2+mg' =qaV_{ac}z_0\sin\omega t+qaV_{ac}\zeta\sin\omega t. \tag{24}$$

This is the equation for the anharmonic oscillator. The modulation has the frequency ω_0.

The modulation shown in figure 4 complicates the evaluation of the observed motion, and a d.c. voltage was therefore not used in such experiments. However, if the drop is lifted by a d.c. field to the midpoint, it can be held stationary, without oscillation, since the vertical a.c. field is zero at the midpoint. As a consequence, pictures may be taken of the drop at a much greater magnification than is possible when the drop oscillates because the field of view must cover the oscillation in the latter case.

4. EXPERIMENTS

Two types of experiments were conducted. In one case the objective was a study of the motion of the suspended drop, specially at the instability. In the other case the variations of mass and charge with time were studied. The same experimental setup was used in both cases. It is shown schematically in figure 5.

The charged drops are injected into the chamber through a hole at 45° to the optical axis. This is accomplished by pressing a rubber bulb connected to a syringe, the needle of which is held at a positive d.c. potential of approximately 3,500 v. A ring-shaped electrode is placed close to the tip of the needle and held at ground potential. The charging of the drop is effected by the field between the needle and the ring. The same hole in the chamber is also used for visual observation of the drop through a microscope.

The suspended drop is illuminated by Koehler illumination and projected onto the film of the camera through a microscope at a magnification of 15.

No camera lens was used. The camera is a Beckman & Whitley Dynafax camera for up to 35,000 f.p.s.

As viewed in the viewing microscope, the drop appears as a vertical line, the length of which is twice the amplitude A, and the midpoint of which is at the coordinate z_0. Numerous drops, varying widely in charge to mass ratio, were suspended in succession. They were held at various levels z_0, and the corresponding values of A were determined. The results are plotted in figure 3. In subsequent experiments the drops were held within the first linear range of this plot.

In order to study the motion of the drop, the drop was suspended at a suitable position, and films were taken at various framing rates. Figure 6 shows a plot of the vertical position of a stable drop as a function of time. The plot is nearly a sine wave with a gradual drift upwards as the drop loses mass by evaporation. Figure 7 shows a corresponding plot for an unstable drop. In this case the drop suddenly moves downwards as a result of a sudden loss of charge. Numerous films of the types shown in figures 6 and 7 were taken, and all gave very similar results.

The dashed curve in figure 7 is an extrapolation of the curve prior to the instability. The dashed curve may be said to represent the motion of the same drop if it had remained stable. The difference between the dashed and the solid curves shows the effect of the instability. This difference is plotted in figure 8. The drop moves initially upwards and then falls toward a new equilibrium position according to an exponential decay curve. The various deviations from the exponential curve are caused by an increase in the amplitude associated with the instability, a detail that was not accounted for when constructing the dashed curve in figure 7. A corresponding plot is shown in figure 9 for the stable drop in figure 6. In this case there is a sudden motion downwards, but the initial equilibrium position is eventually recovered as a result of evaporation.

A sudden change in mass and charge of a suspended drop changes its equation of motion into

$$\ddot{z}+\frac{\beta}{m+\Delta m}\dot{z}+g=\frac{q+\Delta q}{m+\Delta m}aVz\sin\omega t. \tag{25}$$

The path of the drop then starts to deviate by an amount x from the previous path. Initially, when x and $\dot{x}$ are small, we have

$$\ddot{x}=\frac{q+\Delta q}{m+\Delta m}aV(z+x)\sin\omega t-\frac{q}{m}aVz\sin\omega t =\sim\frac{q}{m}aVz\left(\frac{\Delta q}{q}-\frac{\Delta m}{m}\right)\sin\omega t. \tag{26}$$

The sign of $\ddot{x}$ is determined by the signs of $(\Delta q/q-\Delta m/m)$ and $\sin\omega t$. The quantities q, m, a, and V are all positive, and z is negative. The sudden changes observed have all occurred with $\sin\omega t$ positive. Hence,

$$\ddot{x}>0 \text{ if } \frac{\Delta q}{q}-\frac{\Delta m}{m}<0 \tag{27}$$

$$\ddot{x}<0 \text{ if } \frac{\Delta q}{q}-\frac{\Delta m}{m}>0. \tag{28}$$

Δq and Δm are both negative. Hence,

$$\ddot{x}>0 \text{ if } \left|\frac{\Delta q}{q}\right|>\left|\frac{\Delta m}{m}\right| \tag{29}$$

$$\ddot{x}<0 \text{ if } \left|\frac{\Delta q}{q}\right|<\left|\frac{\Delta m}{m}\right|. \tag{30}$$

For an unstable drop $\ddot{x}>0$, and the drop thus loses relatively more charge than mass. For a stable drop $\ddot{x}<0$, and the drop thus loses relatively more mass than charge. The motion of the stable drop thus indicates evaporation

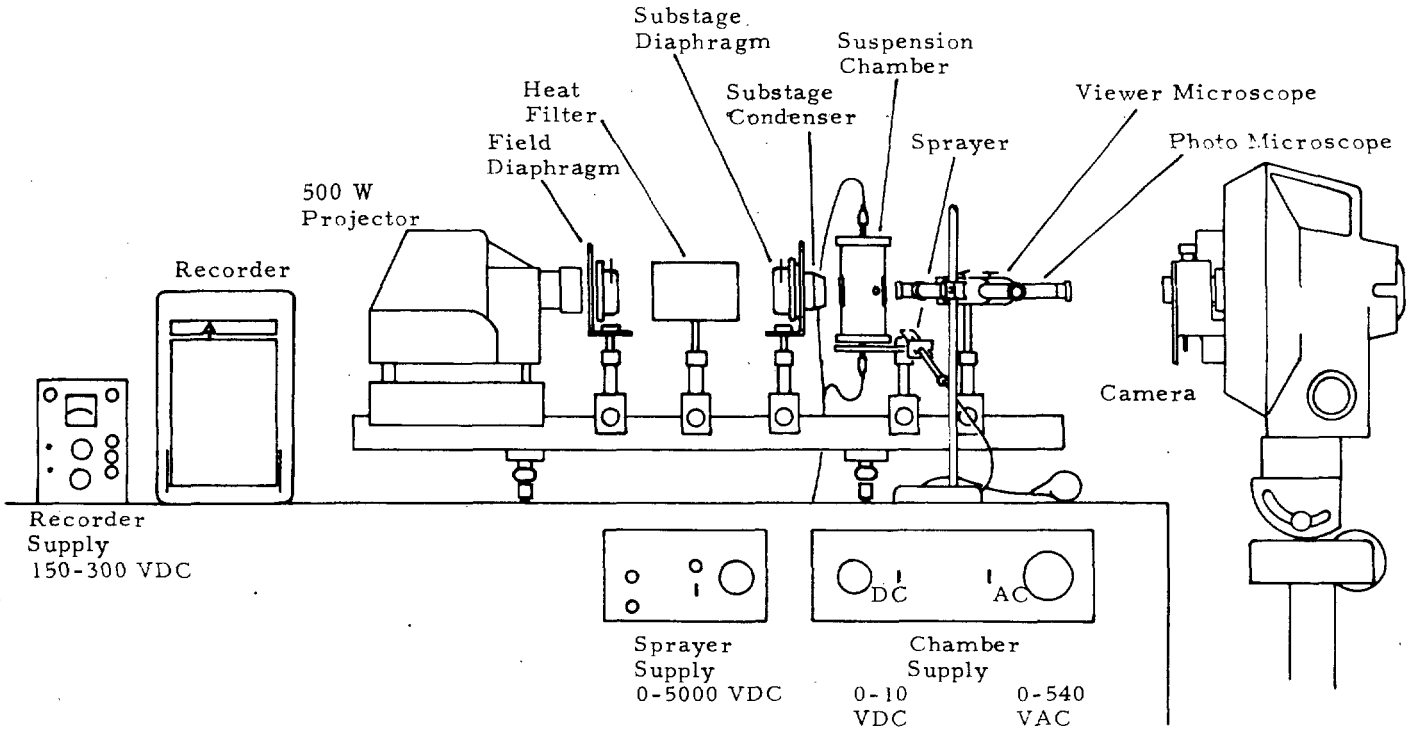

FIGURE 5.—Experimental set up.

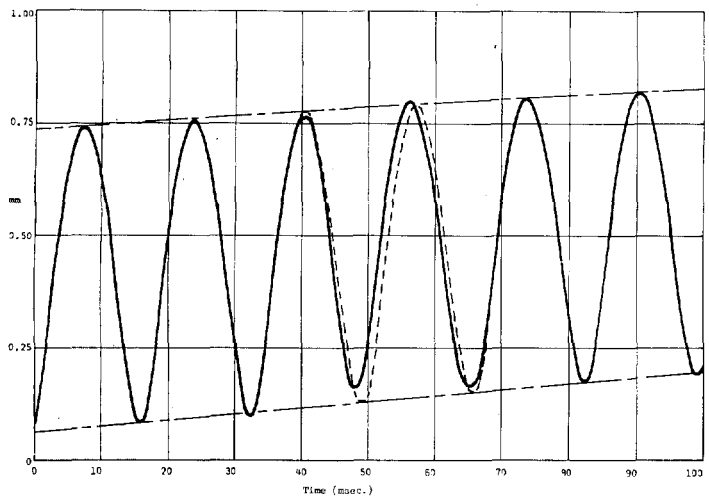

FIGURE 6.—Vertical position of a stable drop in the a.c. field.

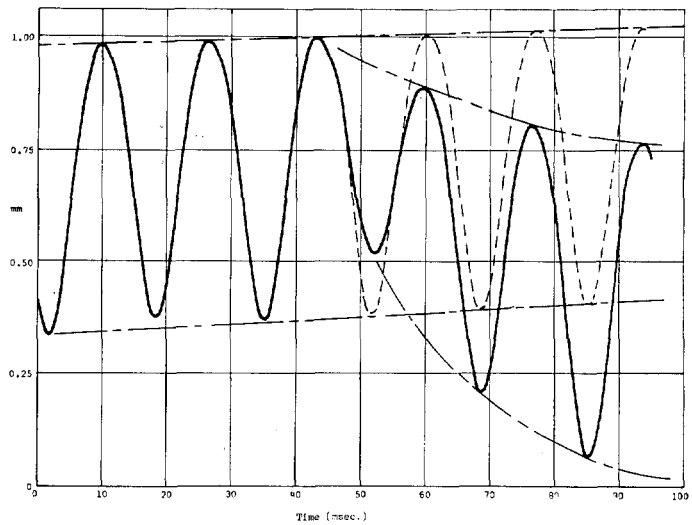

FIGURE 7.—Vertical position of an unstable 40μ drop in the a.c. field.

by spurts or by ejection of small droplets. This subject is discussed further later on.

In order to determine the variations of mass and charge with time for an evaporating drop, a series of measurements were made, in which the drop diameter was measured on the film, and the charge was calculated from the applied a.c. voltage required for holding the drop in a fixed position. To this purpose it is necessary to know the field constant a. This quantity cannot be calculated with adequate accuracy for the electrode configuration used. It was therefore determined empirically. To this end the charge was calculated from formula (1) with the measured drop radius inserted.

The drop was held at a fixed position by adjusting the applied a.c. voltage during the evaporation of the drop. This was done by means of a Variac transformer. The applied a.c. voltage was of the order of a few hundred volts. The voltage was recorded by means of a linear General Radio potentiometer that was mounted on the shaft of the Variac and that was connected to a d.c. voltage. An Esterline-Angus recorder was used.

The drop diameter was measured by taking intermittent photographs of the drop. The time was marked on the voltage record by a spike produced by applying a d.c. pulse. When these photographs were taken, the drop was temporarily lifted to the midpoint by means of a few volts d.c. applied between the two spheres. The horizontal a.c. field was then strong enough to hold the drop sharply in focus, while the vertical a.c. field was too weak to cause appreciable oscillation. As a consequence,

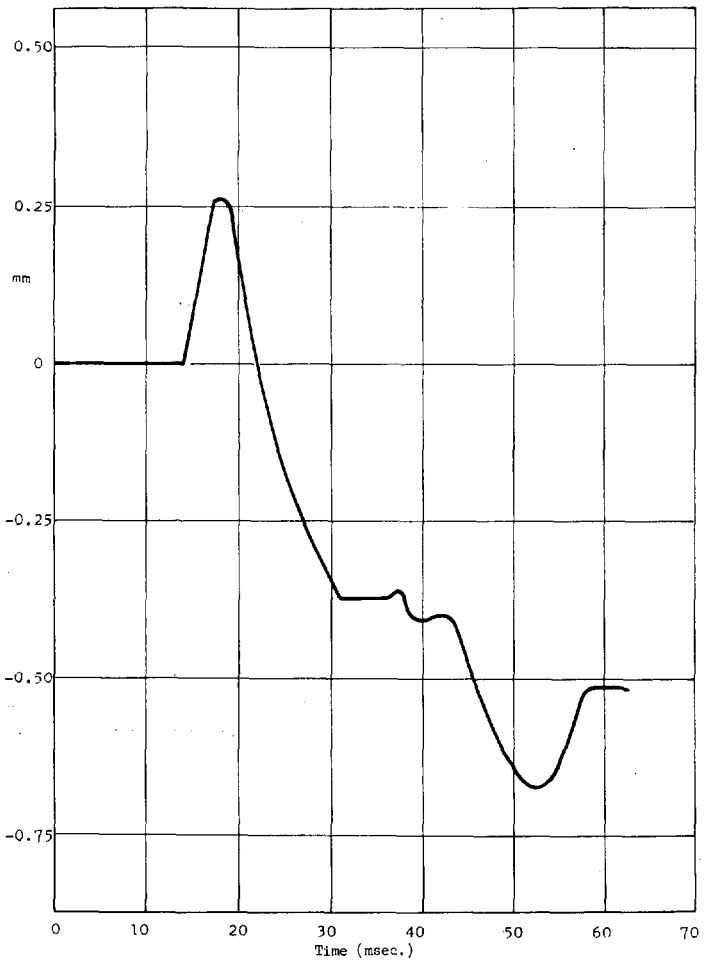

FIGURE 8.—Linearization of the plot in figure 7.

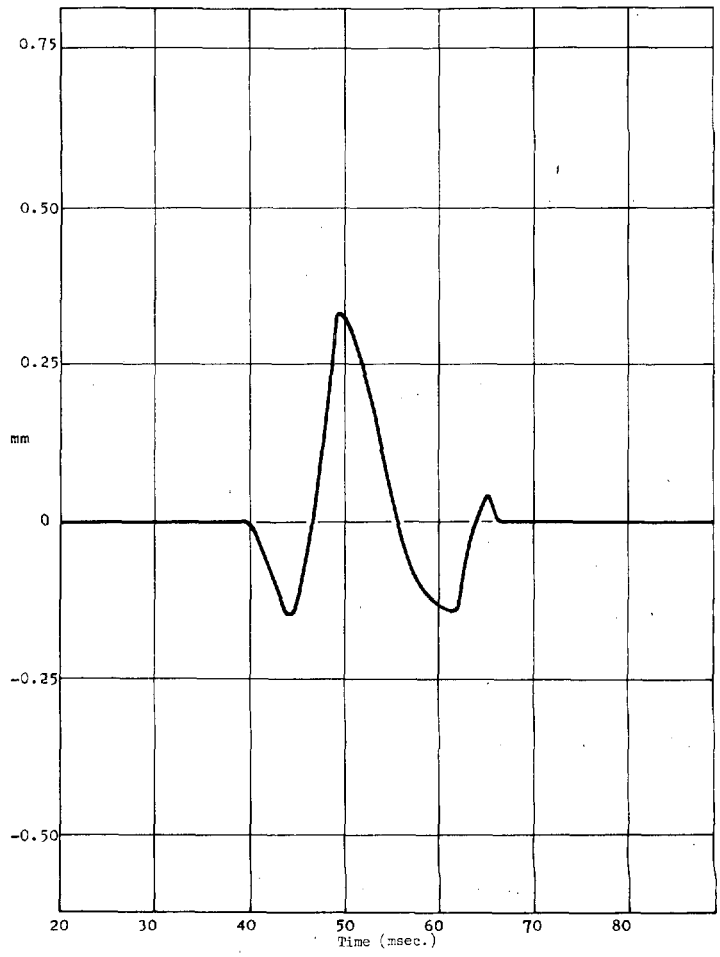

FIGURE 9.—Linearization of the plot in figure 6.

a high magnification, 22, could be used. The film was then projected on a screen at a magnification of 30. The total magnification was thus 660. It is estimated that the error in the measured drop diameter was less than 1 percent.

These measurements were continued until the drop became unstable. The instability was marked by a spike on the record.

Typical plots of d^2 and $V_{ac}^{2/3}$ as functions of time are plotted in figures 10 and 11. Both plots are linear.

According to formula (12), the charge q is proportional to $(d^3/V)\sqrt{1+a^2}$. Plots of this quantity on the data given in figures 10 and 11 are shown in figures 12 and 13.

The results of a series of experiments are presented in table 1. The table gives the drop radius r and the drop charge q at the instability and the rate of evaporation dr^2/dt and the time t from inserting the drop to its instability. The field constant a was calculated from formula (12).

In another series of experiments the d.c. voltage required for holding the drop at the midpoint was determined. The delay between the reading of the a.c. voltage and the exposure of the film for drop size measurement was too large for accurate measurement of the corresponding a.c. voltage. Nevertheless, the a.c. voltage is given together with the d.c. voltage and the drop diameter in figure 14 for comparison. The quantities calculated from the data obtained are listed in table 2. Plots of d^3/V_{ac} and d^3/V_{dc}, which quantities are approximately proportional to q, are given in figure 15.

TABLE 1.—*Data for evaporating and unstable drops*

Run no.	$r_{instab.}$ μ	$q_{instab.}$ e.s.u.	a e.s.u./volt	$\frac{dr^2}{dt}$ cm.²/sec.	$t_{instab.}$ sec.
2	22.4	6.36×10^{-3}	4.44×10^{-3}	10.1×10^{-8}	155
3	29.1	9.42×10^{-3}	4.22×10^{-3}	13.5×10^{-8}	191
4	15.8	3.72×10^{-3}	4.62×10^{-3}	18.0×10^{-8}	70
5	21.8	6.19×10^{-3}	(4.87×10^{-3})	12.3×10^{-8}	116
5	18.9	4.84×10^{-3}	(3.88×10^{-3})	15.7×10^{-8}	116
6	25.2	7.61×10^{-3}	4.44×10^{-3}	10.6×10^{-8}	105
7	21.9	6.17×10^{-3}	4.40×10^{-3}	10.8×10^{-8}	153
8	25.4	7.30×10^{-3}	4.25×10^{-3}	24.5×10^{-8}	69
9	23.6	6.65×10^{-3}	4.44×10^{-3}	8.55×10^{-8}	192

Note: The plot of d^2 against t for Run no. 5 is not linear. Two extreme extrapolated values are given. The average value of a is $a=4.38\times10^{-3}$ e.s.u./volt. Disregarding this value, the average value of a is $a=4.40\times10^{-3}$ e.s.u./volt.

TABLE 2.—*Data for evaporating and unstable drops*

Run no.	$q_{instab.}$ e.s.u.	a' e.s.u./volt	$\frac{dr^2}{dt}$ cm.²/sec.	t sec.
50	6.00×10^{-3}	2.40×10^{-3}	9.63×10^{-8}	143
70	4.16×10^{-3}	2.25×10^{-3}	12.0×10^{-8}	94.5
90	3.93×10^{-3}	2.18×10^{-3}	9.88×10^{-8}	124
110	3.85×10^{-3}	2.06×10^{-3}	11.0×10^{-8}	102
130	5.60×10^{-3}	2.09×10^{-3}	14.0×10^{-8}	97
140	3.72×10^{-3}	2.26×10^{-3}	11.8×10^{-8}	104
Average	.....	2.21×10^{-3}	.....	.....

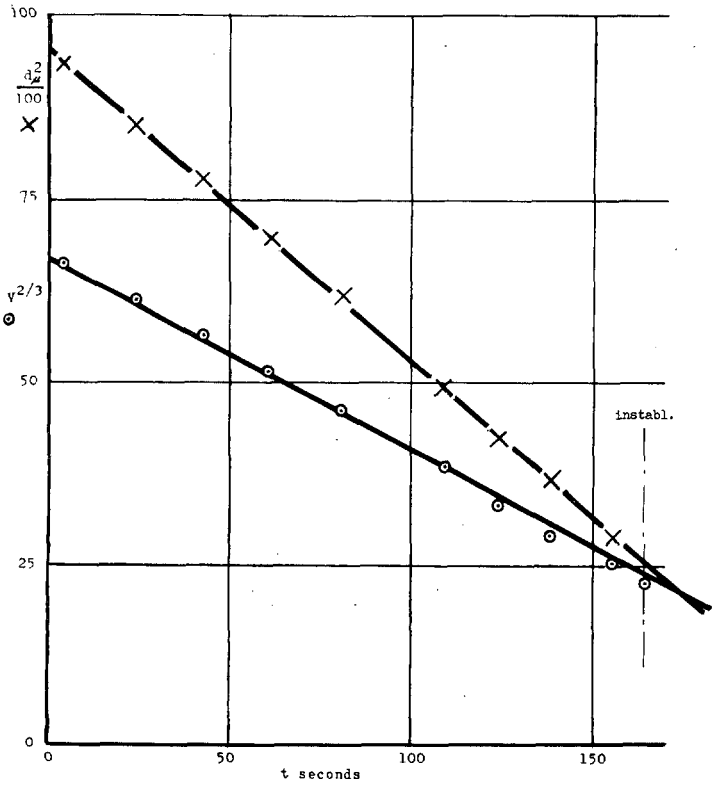

FIGURE 10.—Plots of (drop diameter)^2 and (applied voltage)$^{2/3}$ against time. The plotted values are $\frac{d^2\mu}{100}$ (×) and $V^{2/3}$ (⊙).

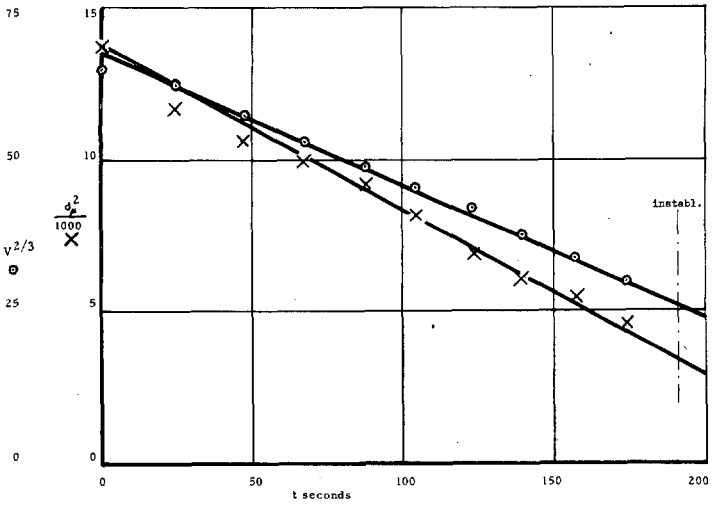

FIGURE 11.—Plots of (drop diameter)^2 and (applied a.c. voltage)$^{2/3}$ against time. The plotted values are $\frac{d^2}{1000}$ (crosses) and $V^{2/3}$ (circled dots).

The experiments just described were all conducted at room temperature and at ambient relative humidity of the air in the suspension chamber. It was noticed that the *rate* of evaporation depended upon the relative humidity, but far less than reported by, e.g., Houghton [9] and Gokhale [4]. There was a great rate of evaporation even when the suspension chamber was flooded and the suspended drop was surrounded by a cloud of condensate droplets.

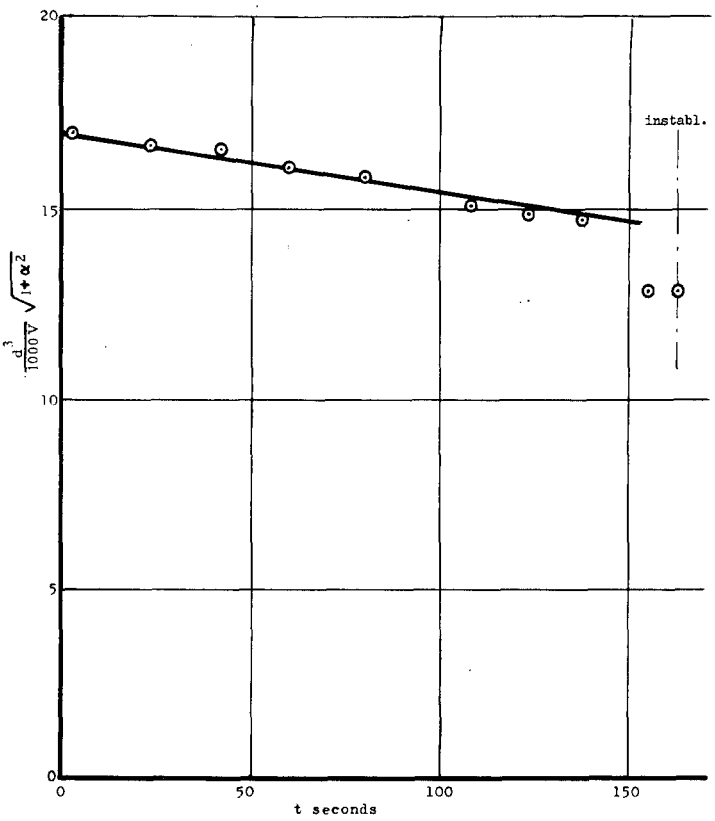

FIGURE 12.—Plot of $\frac{d^3}{V}\sqrt{1+\alpha^2}$ on the data in figure 10.

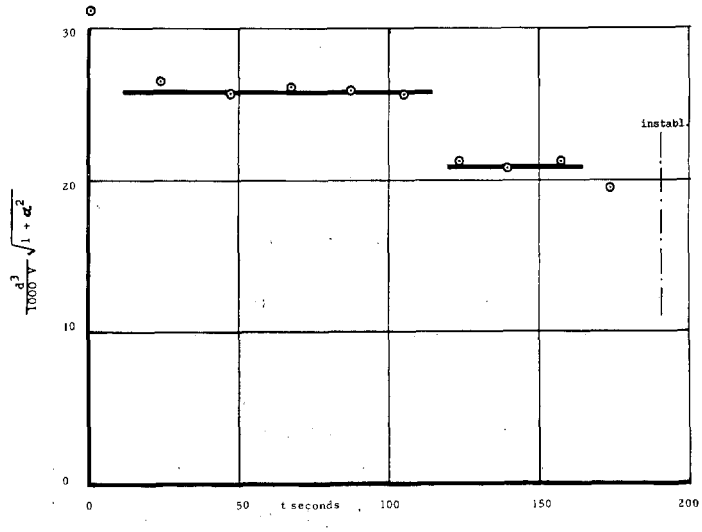

FIGURE 13.—Plot of $\frac{d^3}{V}\sqrt{1+\alpha^2}$ on the data in figure 11.

Other experiments were conducted at controlled temperatures and at a relative humidity close to zero. A drop of room temperature was suspended at −26° C. in the chamber. It evaporated to approximately half its initial size without freezing and exploded after some 30 sec. If the heat of evaporation were all supplied by the water, i.e., if the drop of room temperature remained above −26° C., the water should have been cooled by some

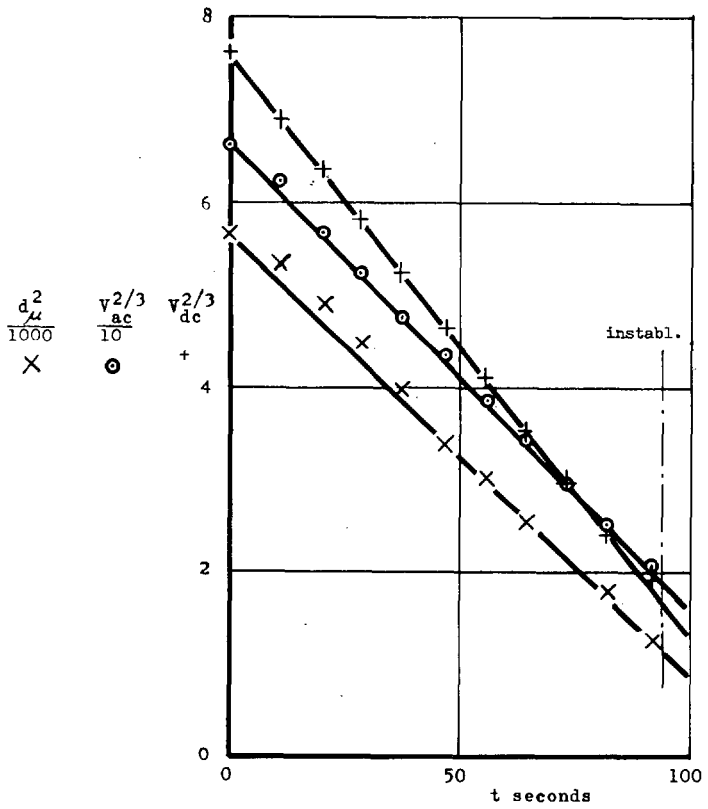

FIGURE 14.—Plots of (drop diameter)^2 (×), (applied a.c. voltage)$^{2/3}$ (⊙), and (applied d.c. voltage)$^{2/3}$ (+) against time.

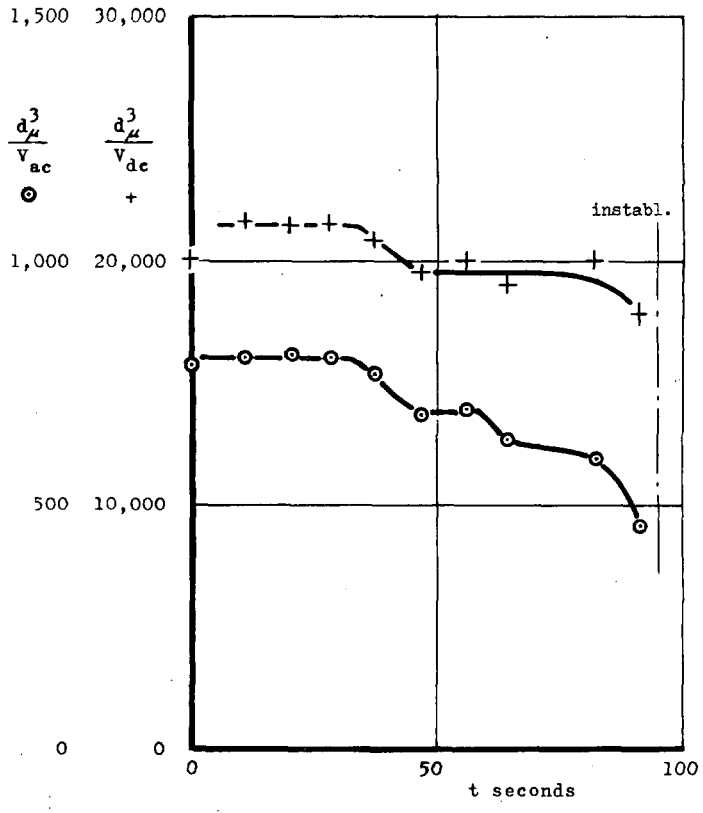

FIGURE 15.—Plots of $\frac{d^3}{V_{ac}}$ (⊙) and $\frac{d^3}{V_{dc}}$ (+) on the data in figure 14.

400° C. The heat transfer between the drop and the air was probably very rapid, and it may well be assumed that the drop had the temperature of the air.

The activation energy for the evaporation was determined by rate measurements at two temperatures, 23° and 0° C. The relative humidity of the air in the suspension chamber was held at approximately zero by means of Drierite. The high temperature was that of the ambient. The low temperature was obtained by means of a cooling coil around the suspension chamber. The temperatures were measured with a mercury thermometer. At the low temperature the hypodermic needle was cooled by holding a piece of ice against it. The water in the syringe was not cooled. The effectiveness of the cooling is shown by the fact that the water occasionally froze at the tip of the needle. It is estimated that the temperature of the drop injected in the suspension chamber was approximately 1° C. Typical data obtained at 0° C. are plotted in figure 16. The results of two series of measurements are presented in table 3.

TABLE 3.—*Data for evaporating and unstable drops*

Run no.	23° C.				0° C.			
	r μ	q e.s.u.	$\frac{dr^2}{dt}$ cm.^{2}/sec.	t sec.	r μ	q e.s.u.	$\frac{dr^2}{dt}$ cm.^{2}/sec.	t sec.
1	26.6	8.62×10^{-3}	2.5×10^{-6}	5.2				
2	21.1	5.95×10^{-3}	2.3×10^{-6}	5.2				
3	21.8	6.25×10^{-3}	2.6×10^{-6}	5.3	26.2	6.84×10^{-3}	0.80×10^{-6}	10.1
4	30.8	10.50×10^{-3}	2.7×10^{-6}	4.5	22.9	6.76×10^{-3}	0.76×10^{-6}	11.7
5	25.8	8.05×10^{-3}	2.75×10^{-6}	5.3	27.5	8.89×10^{-3}	1.22×10^{-6}	12.6
6	24.6	7.50×10^{-3}	2.08×10^{-6}	5.7	22.8	6.71×10^{-3}	1.12×10^{-3}	11.0
7	30.3	10.25×10^{-3}	1.95×10^{-6}	5.9	24.0	7.25×10^{-3}	0.81×10^{-6}	14.1
8	25.0	7.68×10^{-3}	2.15×10^{-6}	5.6	28.5	9.38×10^{-3}	0.90×10^{-6}	15.3
9					26.2	8.27×10^{-3}	0.51×10^{-6}	13.6
10					17.3	1.40×10^{-3}	0.78×10^{-6}	14.6
Average			2.40×10^{-6}				0.86×10^{-6}	

The average rates at the two temperatures inserted in Clapeyron's formula give an activation energy of 7.2 kcal./mole. As already pointed out, the most probable low temperature is 1° rather than 0° C. The most probable value of the activation energy is accordingly 7.6 kcal./mole.

Thousands of unstable drops were observed in these experiments and a great many films were taken, but in no case could any indication of ejected droplets be observed. This is in remarkable contrast to the observations of Doyle, Moffett and Vonnegut [2], and yet we had a vastly superior resolution in space and time by using a microscope and high-speed photography. When all attempts at observing ejected droplets failed, it was concluded that there were no droplets ejected, or that they were too small to be seen, e.g., smalier than 1μ.

It then occurred to us that the droplets observed by Doyle, Moffett, and Vonnegut were not ejected from the unstable drop but condensate droplets formed by nuclei ejected from the unstable drop. They used a large chamber with long diffusion paths to the wall and a high humidity of the air. They might therefore have had some supersaturation of water vapor in the vicinity of the observed drop.

In order to check this hypothesis a sealed suspension chamber was constructed as shown in figure 17. It was

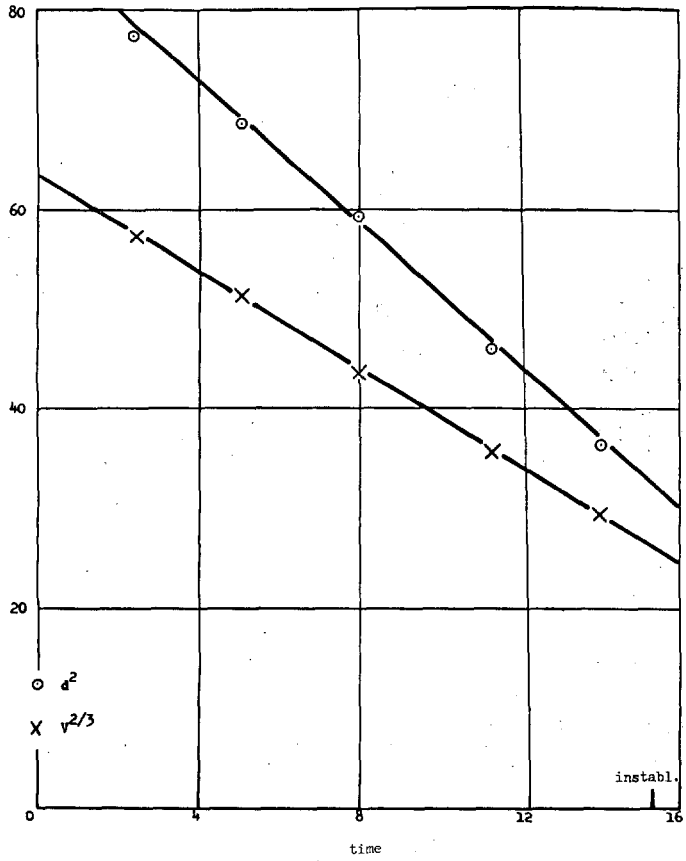

FIGURE 16.—Typical plots of drop diameter and applied voltage at 0° C.

connected to an expansion chamber shown in figure 18. The water level in the pressure chamber is lowered and that in the expansion chamber is raised by increasing the air pressure in the pressure chamber by 100 mm. of mercury. The pressure is then released through a solenoid valve and a needle valve. The duration of the expansion is controlled by setting the needle valve. It was usually approximately 4 sec.

A drop was suspended and watched through the microscope. Shortly after the first instability the solenoid valve was triggered, so that the expanison started and supersaturation was created in the suspension chamber. This state continued over the second instability. At the second instability a burst of small condensate droplets was observed. These observations were made in scattered light at 45° to the optical path. Figure 19 is a reproduction of a photograph taken at an instability. The film was exposed during the duration of the cloud, approximately 1 to 3 sec.

The instability produced a condensate cloud only when there were condensation nuclei present in the air. When the nuclei were removed by repeated expansion, or by filtration of the laboratory air, there was no condensate cloud produced by the instability. The nuclei gave condensate droplets of approximately 5μ in diameter. The droplets produced by the instability were much smaller,

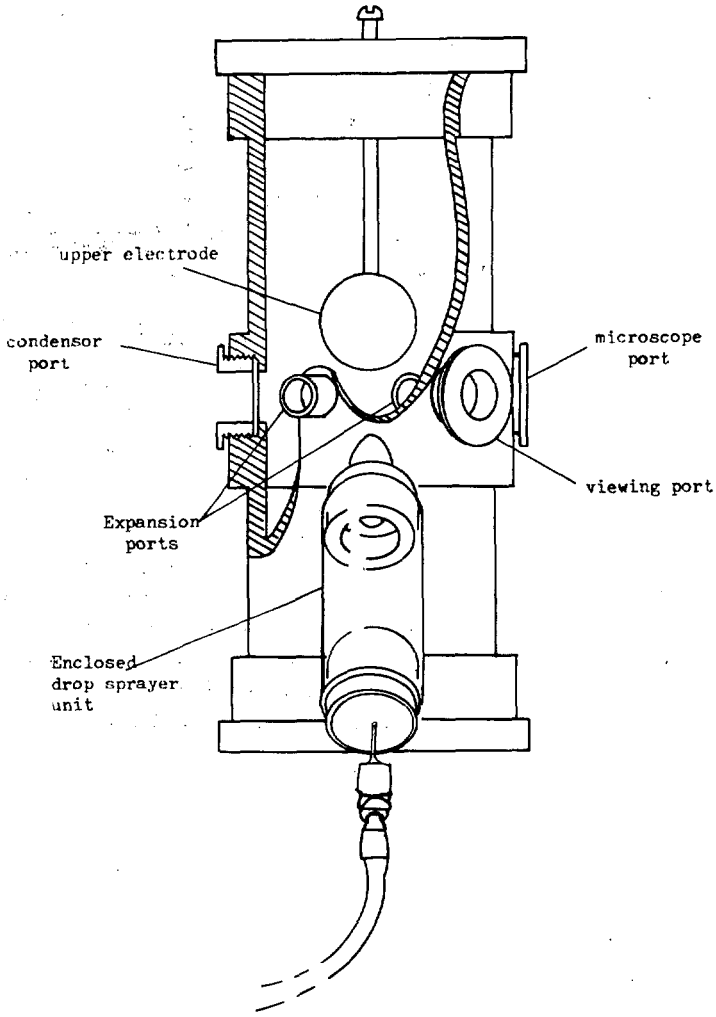

FIGURE 17.—Sealed suspension chamber.

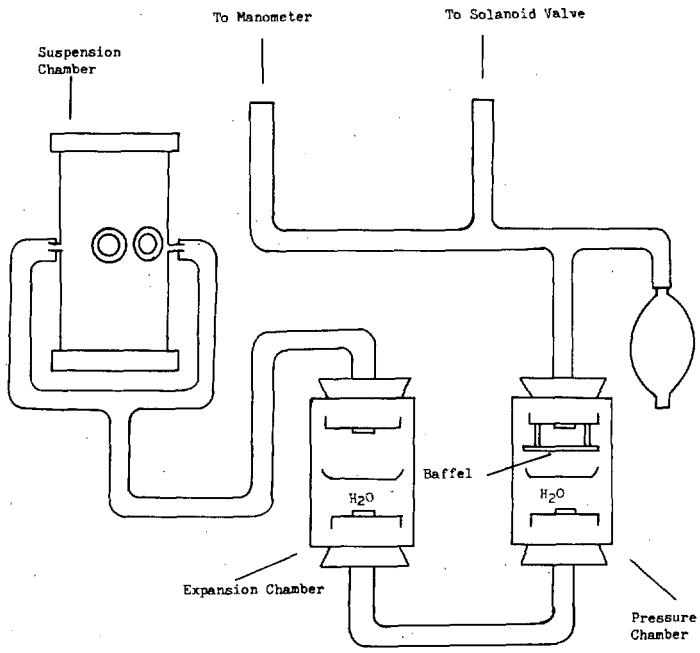

FIGURE 18.—Expansion chamber.

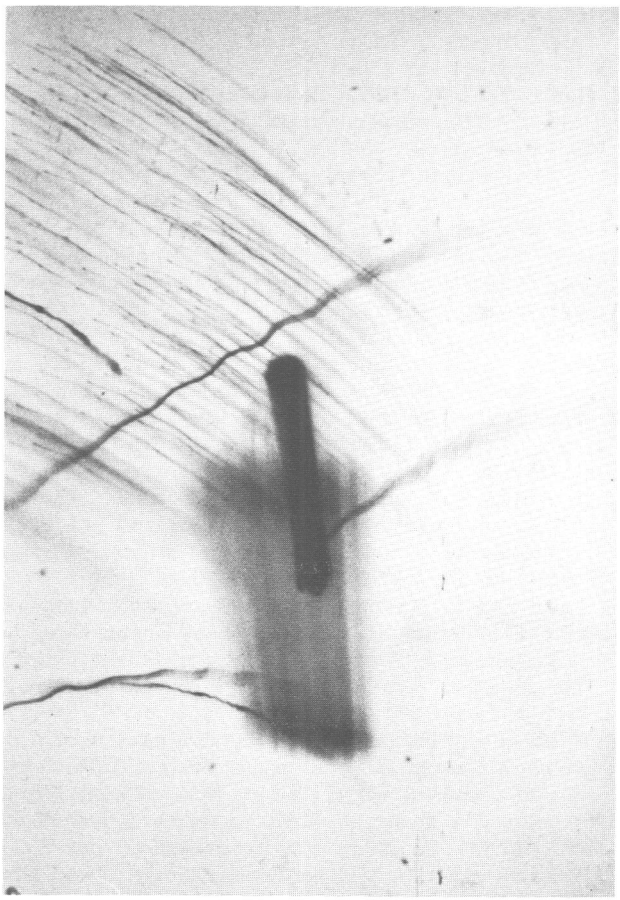

FIGURE 19.—Unstable drop in supersaturated air.

say 2μ in diameter. The two types of droplets were easily distinguished one from the other. There are a few tracks of the large condensate droplets on the photograph.

The identification of the nucleating products of the instability requires some further study, yet to be conducted. It appears, however, that they are molecular rather than particulate since they produce droplets only when nuclei from the air are present. If it may be assumed that the nucleating products of the instability carry the charge lost by the unstable drop, they should then be ions. A remarkable circumstance is that the burst of condensate droplets occurred only under normal weather conditions with a breeze coming in from the sea, but it did not occur when the wind blew from the desert. This may indicate that the ions cause condensation together with NaCl only. One may then speculate that the ions produce NO, the oxidation of which is catalyzed by NaCl and other chlorides.

5. DISCUSSION

The result that dr^2/dt is a constant throughout the period of normal evaporation has been found by several investigators, e.g. [4, 9, 14]. Similar results have been found for the exchange between a water drop and its gaseous environment more generally [10]. The linearity of the plot of $V^{2/3}$ against time was also found by Doyle, Moffett, and Vonnegut [2].

A closer inspection of the data reveals that, in our case, these relations hold only as averages over a sufficient period of time. This is indicated by the large spread in the diameter values in figure 11 as compared to those in figure 10. The plots in figures 12, 13, and 15 show more or less pronounced steps or discontinuities. These may be compared to those in figures 6 and 9 of the path of a stable evaporating drop. All this evidence indicates that the evaporation of a stable charged drop occurs at least partially in the form of bursts under these conditions. The fact that the drop loses charge during the evaporation is indication of ejection of ions or charged droplets since the charge could not be carried by molecules.

The change in charge during evaporation and condensation has been studied by Dubois [3] and Mühleisen [15]. Dubois used drops mounted on spiders' threads. The size of the drop changed slowly over a period of an hour or two and then stopped. The change in charge followed that in size. Mühleisen observed a change in space charge as a result of drying or humidification of a room. Mühleisen's experiments were checked by Knopp [13] and Israël and Knopp [11], who measured the charge in a closed chamber during evaporation of water. They found no change in charge. However, they took pains to exclude electric fields. It thus appears that the loss of charge in evaporation is observable only in the presence of an electric field as in the experiments of ourselves, Dubois, and Mühleisen. But it appears that even very weak fields, such as the atmospheric field, suffice to produce the effect. It is possible, however, that the electrification observed by Dubois and Mühleisen could be caused by drying and humidification of solids present.

Evaporation by spurts has also been observed by Kingdon [12]. His experiments did not distinguish between a spurt of vapor and the ejection of droplets, however. Evaporation by bursts and explosions has been reported by Hickman and Trevoy [8], Hickman [6], and Hickman and Torpey [7] for various liquids, including water, in a vacuum.

The rates of evaporation listed in table 1 are of the same order of magnitude as those reported by other investigators, e.g., Houghton [9] for water and Kracke and Puckett [14] for hexadecane. The rates reported by Gokhale [4] are lower by five or more orders of magnitude. Dubois [3] and Gudris and Kulikowa [5] reported comparatively small rates of evaporation that did not follow the same rate law, and that gradually approached zero in an hour or two.

In the course of the development of the suspension technique we encountered drops that evaporated comparatively slowly and that may be comparable to those used by Dubois and by Gudris and Kulikowa. These drops did not lend themselves to the study of the instability because it was too difficult to synchronize the camera with the event. No rate measurements were made with these drops. The reason for the differences in rates of evaporation is not known.

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The discontinuities observed in the paths of the drops are not attributable to violation of the stability conditions for the suspension. Drops of the size used in our experiments, 30–100μ, then fall out immediately. Several successive instabilities could be observed, and the drop still remained suspended without adjustment of the suspension field.

It is a remarkable fact that the activation energy for the evaporation of water drops has not been determined in the numerous measurements of rates of evaporation reported in the literature. Houghton [9] measured the rate of evaporation at two temperatures, but he corrected his data on the assumption that the evaporation of the drop occurred by the same mechanism and with the same activation energy as in the case of evaporation from the wet bulb thermometer used for the determination of the humidity of the air. The activation energy found in our experiments is not compatible with this assumption.

6. CONCLUSION

The observations reported in this paper as well as observations reported by other investigators show that a water drop may evaporate in spurts. The loss of charge in such a spurt of evaporation or at an instability shows that ions or charged droplets are ejected. The fact that some species ejected by an unstable drop nucleates condensation together with particulate nuclei shows that this species is gaseous. If it may be assumed that the gaseous species also carries the charge lost by the unstable drop, this species must be some ion. The identification of the products of the instability is the objective of continued work. The activation energy, 7.6 kcal./mole, found for this type of evaporation indicates that the removal of water molecules from the drop is not part of the rate-determining step.

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